Rhodium Complexes with Nitrogen-Donor Ligands Anchored on Silicic Supports. 1. Synthesis and Characterization

Pilar Hernan, Carmen del Pino, and Eduardo Ruiz-Hitzky*
Instituto de Ciencia de Materiales, CSIC, c/Serrano 115 bis, 28006 Madrid, Spain
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An amino-functionalized silica, (SiO₂)₂/₃Si(CH₂)₃NH₂ (I) has been synthesized by cohydrolysis of tetraethoxysilicate (TEOS) and (3-aminopropyl)triethoxysilane (APS), following an acid-catalyzed sol–gel process. The primary amine functions of I, by reaction with diketones or pyridine-2-carboxaldehyde, create "in situ" diazabutadiene (R-DAB) or pyrrolecarbimine (R-PyCa) ligands grafted to the silicic support. By subsequent reaction of these N-donor groups with RhCl₃·3H₂O or various organometallic complexes of rhodium, we have obtained anchored rhodium complexes homogeneously dispersed on the silicic support. The results obtained by this route have been compared with those obtained by forming first the rhodium complex with a ligand derivative from R-propyltriethoxysilane (R = amine, DAB, PyCa) and its subsequent copolymerization with TEOS. Some experiments with silica gel (Kieselgel-60) carried out in parallel have enabled us to study the differences between this silica matrix and that generated from TEOS. These organo-inorganic materials were characterized by elemental analysis, TEM-EDX technique and IR, CP-MAS ¹³C NMR, and XPS spectroscopy.

Introduction

The development of materials based on modification of silica by the grafting or organosilanes or transition-metal species has been receiving increasing attention due to their potential use in different applications, mainly as chromatographic supports¹ and as solid matrices to anchor soluble catalysts.² In this last approach the supported catalysts combine the advantages of homogeneous and heterogeneous catalysis. The design and preparation of stable organo-inorganic systems, nanocomposites, containing functional groups, would permit changes in their topology by altering the reaction conditions and, consequently, would make it possible to obtain "new" materials, or old materials with new properties.³

Supports functionalized with mono- or bidentate phosphine ligands have been intensively studied;⁴ on the contrary functionalization with N-donor ligands has not been so well investigated.

A critical problem associated with the anchoring of metal complexes is the loss (leaching) of the metal if the ligands by which the metal is attached to the support are involved in dissociation equilibria.⁴ There are different ways to reduce this disadvantage in these materials: (a) The increase of the ligand concentration in the support; (b) the use of microporous matrices; (c) the use of chelating ligands.⁵

The present work is concerned with the preparation of a series of rhodium complexes anchored to silica functionalized with various chelating N-donor groups; the support in this case is robust microporous and three dimensional. We have used low metal loading in the hope of avoiding leaching when we use these materials as supported catalysts.

Experimental Section

Materials. RhCl₃·3H₂O (Johnson Matthey C.L.) was used without purification.

Scheme I. Procedure for the Preparation of Silica Functionalized with N-Donor Groups: (i) -NH₂

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Scheme II. Rhodium Complexes Anchored on Silica Functionalized with N-Donor Groups

![Diagram of Rhodium Complexes Anchored on Silica Functionalized with N-Donor Groups]

(a) Reaction of I with RhCl₃·3H₂O: RhCl₃·3H₂O (0.03 g) in methanol was added to a suspension of I in MeOH (0.050 g/25 mL), and the mixture was stirred at 25 °C for 3 days. The resulting orange-red solid was filtered, carefully washed with MeOH to eliminate the excess uncomplexed rhodium chloride, and vacuum dried at room temperature.

(b) Reaction of I with other Rh complexes: In a manner similar to that described above, compound I was treated with the following Rh complexes: [Rh(CO)₃]₃, prepared by heating RhCl₃·3H₂O in a CO stream; [RhCl(COD)]₂, obtained by reaction of RhCl₃·3H₂O with COD (cyclooctadiene) in EtOH and heated to reflux for 3 h in a N₂ atmosphere; RhCl(CO)(P₂Et₄), prepared by reaction of [RhCl(COD)]₂, with P₂Et₄, in toluene. 

(c,d) Reaction of I with TEOS, RhCl₃·3H₂O and [RhCl(COD)]₂: The procedure was the same as described above in (a) and (b), respectively.

In all cases the reaction period of the support with the complex was 3 days (at 25 °C) and the stoichiometric ratio N/Rh was always in the range 1~2 (N calculated from elemental analysis of the functionalized support).

(3) Formation of Rhodium Complexes ([Rh] with Triethoxysilyl Ligands (Scheme II, Route 2). [Rh] means the various Rh compounds studied RhCl₃·3H₂O, [RhCl(COD)]₂, [RhCl(COD)]₃, and RhCl(CO)(P₂Et₄).

(a) Reaction of APS with [Rh] and TEOS. APS (4 mmol) was treated with [Rh] (1~4 mmol) in ethanol and stirred at room temperature for 4 h. The jelled product was treated with a partially hydrolyzed solution of TEOS; the mixture was stirred for 2 days, extracted in a Soxhlet apparatus with CH₂Cl₂ and dried at 70 °C for 2 h. The resulting solid was orange.

The partial hydrolysis of TEOS was carried out in a separate reaction flask for 4 h in a mixture of 1.4 mL of TEOS, 30 mL of ethanol, 1 mL of H₂O, and a drop of HCl.

(b) Reaction of APS with Diacetyl, [Rh], and TEOS. APS (4 mmol) was allowed to react with diacetyl (2 mmol) in toluene during 18 h of stirring. The resulting o-dilin ligand was made to react with the rhodium compound at room temperature for 4 h with stirring. As the ethylox groups of APS hydrolyze more quickly than TEOS, a partially hydrolyzed solution of the latter was added to an ethanolic suspension of the rhodium R-DAB complex (R = triethoxysilyl). The process follows as previously described.

(c) Reaction of APS with Benzil, [Rh], and TEOS. APS (4 mmol) was made to react with benzil (2 mmol) in toluene, with stirring for 18 h. This APS, functionalized with the benzilidazenedi ligand and dissolved in 30 mL of ethanol, was allowed to react with the rhodium compound as before; partially hydrolyzed TEOS was added, as above, to give an off-white product.

(d) Reaction of APS with Pyridine-2-carboxaldehyde, [Rh], and TEOS. A solution of pyridine-2-carboxaldehyde in benzene was added to APS solution in the same solvent. The molar ratio of reactants was 1/1. The reaction mixture was kept at 0 °C with stirring. After 1 h the reaction was complete, and the jelled product was filtered off, washed with acetone and vacuum dried. The metal loading was as described before and finally treated with partially hydrolyzed TEOS.

Techniques. Microanalyses were performed on a Perkin-Elmer Model 380C elemental analyzer for C, H, and N. Rhodium was determined by atomic absorption in a PYE UNICAM spectrophotometer after decomposition of the sample with HF:HNO₃ (2:1). IR spectra were recorded in the range 4000~250 cm⁻¹, using KBr disks, fluorolube, or Nujol mulls, on a Perkin-Elmer 580B spectrophotometer, coupled to a M-3500 data station.

The ¹H solid-state NMR spectra were obtained in a Varian XL-200 MHz equipped with a 3000 Aspect computer with Fourier transform. The instrument settings were as follows: 90° pulse width for Hₐ and H₈, 3 x 10⁻⁸ s; spectra width 10 kHz; acquisition time 0.05 s; proton decoupling power 20 G; sample spinning speed 2.1 kHz; contact time 10⁻⁸ s; time delay between scans, 3 s.

Rhodium Complexes with N-Donor Ligands

transmission electron microscopy (TEM), on a Siemens Elmiscop
are referred
spectrophotometer and
monochromated radiation. All reported binding energies (BE)
LHSlO
Carlo Erba Strumentazione Sorptomatic
a Philips EM
APS:EtOH:H2O of 4:1:16:32.6a The gel obtained after
carried out by cohydrolysis of tetra-
groups/g of substrate as estimated from the elemental
drying at 110
analysis. It exhibits good homogeneity in the shape and
size
silane
and pore volume are 107 m2/g and 0.43 cm3/g, respectively.
created heterodiazabutadiene (R-DAB, -N=C-C=)
functions (I) was carried out by cohydrolysis of tetra-
ethylorthosilicate (TEOS) and
functions, -NH2, -DAB, and -PyCa, should be
able to coordinate to rhodium compounds to give sur-
face-anchored complexes (Scheme 11).
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anchoring of the soluble Rh compound ({Rh}) to the
complex containing N-donor ligand attached to a trieth-
oxisilyl function, followed by cohydrolysis with TEOS.
Two alternative routes have been followed: route 1,
anchoring of the soluble Rh compound ([Rh]) to the
functionalized silica; route 2, formation of the rhodium
complexes, three different procedures have been followed.
In Table I we have chosen some representative examples:
the metal is well dispersed on the function-
contact with the silica does not take place, we have tested the reaction of

XPS measurements were carried out on a Leybold Heraeus
LHS10 spectrometer, employing Mg Kα (hv = 1253.6 eV)
non-
monochromated radiation. All reported binding energies (BE)
are referred
to the carbon signal C1s (284.6 eV).
The morphology of the samples was determined by direct
transmission electron microscopy (TEM), on a Siemens Elmiscop
102. The chemical homogeneity of the particles was observed with
a Philips EM 420 microscope with an energy-dispersive X-ray
spectrophotometer and an EDAX 9100 analyzer computer system.
The specific surface area (BET, N2) of compound 1 (silica
functionalized with aminopropyl groups) was determined on a
Carlo Erba Strumentazione Sorptomatic 1800 instrument, using a
Milestone 100 program.

Results and Discussion
The preparation of a silica matrix containing NH2
functions (I) was carried out by cohydrolysis of tetra-
ethylorthosilicate (TEOS) and (3-aminopropyl)triethoxy-
silane (APS) following a conventional acid-catalyzed sol–gel processc (Scheme II) from a molar proportion of TEOS:
APS:EtOH:H2O of 4:1:16:32. The gel obtained after
drying at 110 °C has a content of 2.7 mmol of aminopropyl
groups/g of substrate as estimated from the elemental
analysis. It exhibits good homogeneity in the shape and
size of the particles, which are present as connected spheres
of about 20-nm diameter, as evidenced by electron micro-
scopy (Figure 1A). The specific surface area (BET, N2)
and pore volume are 107 m2/g and 0.43 cm3/g, respectively.
The presence of free primary amine functions will allow
their subsequent reaction with dicarbonyl compounds,
(RCOCOR, R = CH3, C6H5; Scheme iii) and with pyri-
dine-2-carboxaldehyde (NC2H4CHO, Scheme iii) in order to
create heterodiazabutadiene (R-DAB, -N=N=C=C−
N—), and pyridine-2-carbimine (R-PyCa, 2-C5H4NC−
(H)−N−) functions, respectively. The three types of
N-donor functions, -NH2, -DAB, and -PyCa, should be
able to coordinate to rhodium compounds to give sur-
face-anchored complexes (Scheme II).
Two alternative routes have been followed: route 1,
anchoring of the soluble Rh compound ([Rh]) to the
functionalized silica; route 2, formation of the rhodium
complex containing N-donor ligand attached to a trieth-
oxisilyl function, followed by cohydrolysis with TEOS.
Route 1. For the preparation of rhodium-supported
complexes, three different procedures have been followed.
In Table I we have chosen some representative examples:
(i) direct reaction of the halide (compounds 1–3), (ii)
displacement of a ligand of the soluble complex for the
N-donor ligand attached to the silica (compound 4, elim-
ination of phosphine); (iii) bridge cleavage of a dimer such as
[RhCl(CO)3]2 and [RhCl(COD)]2 (compounds 5 and 6),
according to the equation

\[
\begin{align*}
Y \text{RhCl} + 2 \text{L} & \rightarrow \text{Y} \text{RhClL2} \\
2 \text{Y} \text{RhCl} + 4 \text{L} & \rightarrow \text{Y} \text{RhClL4}
\end{align*}
\]

where L represents a monodentate grafted N function on
the silica (−NH2), and LL the chelating functions DAB and
PyCa; Y and YY represent CO and COD, respectively.
The loading of rhodium was carried out in methanol or
toluene at 25 °C, with stirring for 3 days.9 In the resulting
compounds, the metal is well dispersed on the functional-
ized support as is revealed by the homogeneous dotting
shown in the photomicrograph B (Figure 1) of sample 6
[I + [RhCl(COD)]2, rhodium, as Rh+, content 6.18; Table
1], which has been selected as an illustrative example.
Spots and average TEM-EDX analyses realized on ran-
domly selected particles show good homogeneity of rho-
dium distribution.

To be sure that rhodium coordinates to the N-donor
functions and that attachment to the silanol groups of the
silica does not take place, we have tested the reaction of

Table I. Analytical Data of the Compounds Obtained by Reaction of I+ or I0 with Different Rhodium Compounds (Scheme II, Route 1)

<table>
<thead>
<tr>
<th>compound</th>
<th>color</th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
<th>% Rh</th>
<th>C/N</th>
<th>N/Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>white</td>
<td>10.71</td>
<td>3.19</td>
<td>3.78</td>
<td>3.3 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1, I + RhCl3⋅3H2O</td>
<td>orange</td>
<td>10.60</td>
<td>2.76</td>
<td>3.18</td>
<td>3.45</td>
<td>3.8 (3)</td>
<td>6.8</td>
</tr>
<tr>
<td>2, I0 + RhCl3⋅3H2O</td>
<td>orange</td>
<td>10.97</td>
<td>2.67</td>
<td>3.39</td>
<td>2.44</td>
<td>3.8 (5)</td>
<td>10.2</td>
</tr>
<tr>
<td>3, I0 + RhCl3⋅3H2O</td>
<td>orange</td>
<td>15.05</td>
<td>3.97</td>
<td>3.20</td>
<td>2.74</td>
<td>5.5 (10)</td>
<td>8.6</td>
</tr>
<tr>
<td>4, I + RhCl(CO)(PEt3)2</td>
<td>pale yellow</td>
<td>14.19</td>
<td>3.32</td>
<td>3.57</td>
<td>3.11</td>
<td>4.9</td>
<td>8.0</td>
</tr>
<tr>
<td>5, I + [RhCl(COD)2]2</td>
<td>pale yellow</td>
<td>12.13</td>
<td>2.97</td>
<td>3.09</td>
<td>3.32</td>
<td>4.6</td>
<td>5.8</td>
</tr>
<tr>
<td>6, I + [RhCl(COD)2]2</td>
<td>cream</td>
<td>12.25</td>
<td>2.89</td>
<td>3.27</td>
<td>6.18</td>
<td>4.4</td>
<td>3.9</td>
</tr>
</tbody>
</table>

*a = (SiO2)1/3Si(CH3)2NH3. b Silica functionalized with diazadiene groups. c Experimental (calculated). d I + diacetyl. e I + benzil.

Figure 1. TEM photomicrographs: (A) silica functionalized with
NH2 groups (I, 300 000); (B) I after anchoring [RhCl(CO)3]2
(×370 000).

(9) Allum, K. G.; Hancock, R. D.; Howell, I. V.; McKenzie, S.; Pite-
silica gel with rhodium compounds under the same reaction conditions (3 days, room temperature). The sample was washed with methanol, and a white silica and orange solution was obtained. No rhodium was detected in the silica (by atomic absorption or fluorescence analyses).

Experiments at different N/Rh ratios in the interval 1-2 have shown that the effective loading is lower than the theoretical value proposed in Scheme II (a ratio of 2N/Rh); to increase the amount of rhodium fixed on the sample, a higher initial concentration of rhodium, higher temperature, and longer periods of reaction would have been necessary, but we have intentionally followed very mild reaction conditions to be sure that the coordination around the metal is the same as in solution.$^{2a,3}$ In this first part of our work, we have not tried to get a maximum metal loading$^{c}$ because we are proposing to try these materials as catalysts, with a surface loading of metal of 1-2 Rh/100 Å², well dispersed and firmly attached to the support.

Although we have chosen 3 days as the standard reaction time at room temperature, we have studied the effect that the increasing time of reaction up to 40 days has on the oxidation state of the metal if the solvent is an alcohol, (either ethanol or methanol, able to act as reducing agent on Rh$^{a+}$ (Figure 2); the reduction Rh$^{a+} \rightarrow$ Rh$^{+} \rightarrow$ Rh is accompanied by a progressive change in color from orange to dark grey. The increasing amount of reduced rhodium has been confirmed by XPS spectroscopy (Figure 2). The XPS data reported in the literature for the different oxidation states of Rh for the level 3d$_{3/2}$ and 3d$_{5/2}$ are Rh$^{a+}$ = 312.1 and 307.2 eV, Rh$^{a+}$ = 312.5 and 307.8 eV, Rh$^{3+}$ = 315 and 310.3 eV.$^{10}$ According to our results, the Rh$^{3+}$ of the RhCl$_3$-3H$_2$O is reduced by the alcohol to Rh$^{+}$, which is the predominant species in the reaction product, but prolonged contact with the alcohol produces some Rh$^{a+}$.

The fact is consistent with the color of the sample and the appearance of a shoulder in the XPS spectra on the side of lower binding energy (samples b and c).

When the experimental C/N ratio is higher than the theoretical one, it is attributed to the presence of methoxy or ethoxy groups, either not hydrolyzed or incorporated from the alcoholic medium (see compound I, Table I). The percentage of C in a compound allows us to determine the number of C atoms attached to the functional group, and the experimental C/N ratio compared with the theoretical one tells us whether or not the reaction of amine groups with the diketone (diacetyl or benzil) or the aldehyde (pyridine-2-carboxaldehyde) has been completed (compounds 2 and 3, Table I).

In these systems, it is necessary to define rigorously the reaction conditions as the variation of any one of them may change considerably the nature of the reaction product. See, for example, Table II, where we have compared the results obtained using an aqueous solution with those obtained in an alcholic one. In an aqueous medium, the amount of rhodium fixed is higher than in alcohol. When the reaction takes place in water, a loss of ligands occurs, possibly due to the removal of soluble oligomeric siloxanes$^g$ that are formed by self-condensation reactions. As a consequence of this an easier fixation of rhodium and a lower N/Rh ratio occur.

**Table II. Influence of the Solvent on the Reaction Products**

<table>
<thead>
<tr>
<th>compound</th>
<th>color</th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
<th>% Rh</th>
<th>C/N$^a$</th>
<th>N/Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td>I, $I^*$ + RhCl$_3$-3H$_2$O (alcohol)</td>
<td>orange</td>
<td>10.60</td>
<td>2.76</td>
<td>3.18</td>
<td>3.45</td>
<td>3.8 (3)</td>
<td>6.8</td>
</tr>
<tr>
<td>1', $I'$ + RhCl$_3$-3H$_2$O (water)</td>
<td>mauve-gray</td>
<td>7.80</td>
<td>2.33</td>
<td>2.91</td>
<td>4.82</td>
<td>3.1 (3)</td>
<td>4.4</td>
</tr>
</tbody>
</table>

*a Experimental (calculated).*

Figure 2. Binding energy for Rh$_{3d}$ levels after increasing periods of reaction. 1 + RhCl$_3$-3H$_2$O: (a) 3 days, (b) 6 days, (c) 10 days. The reaction conditions (3 days, room temperature). The sample was washed with methanol, and a white silica and orange solution was obtained. No rhodium was detected in the silica (by atomic absorption or fluorescence analyses).
Rhodium Complexes with N-Donor Ligands

Figure 3. Infrared spectra of the silane APS (EtO)₃Si(CH₂)₃NH₂ (A) and its reaction products with diacetyl (B), benzil (C), and 2-pyridinecarboxaldehyde (D).

Figure 4. CP-MAS ¹³C NMR spectra: (a) APS + D, i.e., (EtO)₃Si(CH₂)₃NH₂ + CH₃COCOCH₃; (b) APS + B, i.e., (EtO)₃Si(CH₂)₃NH₂ + C₆H₅COCOC₆H₅.

bands of R-DAB or R-PyCa ligands are observed when the corresponding silica derivatives are treated with the [Rh] rhodium compounds. Besides, it is known that the ν-(N≡C) stretching bands are not very sensitive to any modification in either frequency or intensity when electronic environment changes affecting these imino bonds take place.

In Figures 4 and 5, it can be seen that high-resolution ¹³C solid-state CP-MAS NMR spectroscopy provides useful information on the reaction of APS with diketones, as well as on the formation of the complexes with rhodium species. One can observe the presence of the methylene groups of the propyl chain (C₁-C₃) which appear at 12-13, 23-26 and 57-59 ppm, respectively. The signals at 167 and 168 ppm can be assigned to the imine carbons (C₅). The phenyl groups in the benzil derivative show signals in the 130-140 ppm range, whereas the remaining CO groups in these compounds are identified by the signal at 200 ppm (Cₛ). The unreacted NH₂ groups (C₆) give peaks at 46-47 ppm, indicating the presence of some free primary diketones. Low-intensity signals at 20-21 ppm can be attributed to nonhydrolyzed ethoxy groups remaining in the support.

The coordination between N-donor groups and Rh³⁺ can be inferred from the shifts detected in the ¹³C NMR signals corresponding to C(4) nuclei, both before and after formation of the supported complexes. Figure 5 shows, as an example, the corresponding spectra of compounds (APS


Table III. Analytical Data of Some of the Compounds Formed before and after Being Supported According to Route 2

<table>
<thead>
<tr>
<th>compound</th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
<th>% Rh</th>
<th>C/N*</th>
<th>N/Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, APSB + Bc</td>
<td>50.46</td>
<td>6.02</td>
<td>6.08</td>
<td>9.7 (10)</td>
<td>54.90</td>
<td>7.12</td>
</tr>
<tr>
<td>2, APS + RhCl₃ (route 2)</td>
<td>37.25</td>
<td>5.19</td>
<td>4.15</td>
<td>10.5 (10)</td>
<td>37.25</td>
<td>2.84</td>
</tr>
<tr>
<td>3, APS + RhCl₃·3H₂O</td>
<td>32.94</td>
<td>4.19</td>
<td>3.82</td>
<td>3.65</td>
<td>10.1 (10)</td>
<td>7.7</td>
</tr>
<tr>
<td>4, APS + RhCl₃·3H₂O</td>
<td>44.45</td>
<td>4.87</td>
<td>5.01</td>
<td>10.03</td>
<td>10.3 (10)</td>
<td>3.7</td>
</tr>
<tr>
<td>5, APS + D' + TEOS</td>
<td>35.50</td>
<td>6.50</td>
<td>8.40</td>
<td>4.9 (5)</td>
<td>5.1 (5)</td>
<td>190</td>
</tr>
<tr>
<td>6, 11 + RhCl₃·3H₂O</td>
<td>34.60</td>
<td>5.80</td>
<td>6.90</td>
<td>0.26</td>
<td>5.1 (5)</td>
<td>190</td>
</tr>
</tbody>
</table>

*aExperimental (calculated). *bAPS = (3-aminopropyl)triethoxysilane. *cB = benzil (C₆H₅COCOCH₃). *dTetraethylorthosilicate ((OEt)₄Si). *dD = diacetyl (CH₃COCOCH₃).

Table IV. Example of the Different Composition Obtained According to the Route Followed

<table>
<thead>
<tr>
<th>compound</th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
<th>% Rh</th>
<th>C/N</th>
<th>N/Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td>3, I + B + RhCl₃·3H₂O</td>
<td>15.06</td>
<td>3.97</td>
<td>3.20</td>
<td>2.74</td>
<td>5.5 (10)</td>
<td>8.6</td>
</tr>
<tr>
<td>9, APS + B + TEOS + RhCl₃·3H₂O</td>
<td>32.94</td>
<td>4.19</td>
<td>3.82</td>
<td>3.65</td>
<td>10.1 (10)</td>
<td>7.7</td>
</tr>
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</table>

Table V. Values of the Binding Energies (eV) of Some of the Complexes Investigated

<table>
<thead>
<tr>
<th>compound</th>
<th>C₁s</th>
<th>O₁s</th>
<th>Si₂p</th>
<th>N₁s</th>
<th>Cl₂p</th>
<th>d₃/₂</th>
<th>d₅/₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>APS + D'B</td>
<td>284.6</td>
<td>351.7</td>
<td>101.9</td>
<td>988.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>APS + B'B (7)'</td>
<td>284.6</td>
<td>351.9</td>
<td>102.9</td>
<td>988.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>APS + RhCl₃</td>
<td>284.6</td>
<td>250.0</td>
<td>102.1</td>
<td>989.6</td>
<td>197.6</td>
<td>313.5</td>
<td>308.6</td>
</tr>
<tr>
<td>APS + D + RhCl₃</td>
<td>284.6</td>
<td>251.5</td>
<td>101.9</td>
<td>989.6</td>
<td>197.7</td>
<td>313.9</td>
<td>309.0</td>
</tr>
<tr>
<td>APS + D + RhCl₃ (10)'</td>
<td>284.6</td>
<td>252.5</td>
<td>102.4</td>
<td>989.5</td>
<td>198.4</td>
<td>313.7</td>
<td>308.8</td>
</tr>
<tr>
<td>APS + D + TEOS + RhCl₃ (12)'</td>
<td>284.6</td>
<td>252.6</td>
<td>102.5</td>
<td>989.7</td>
<td>198.4</td>
<td>313.5</td>
<td>308.9</td>
</tr>
<tr>
<td>APS + B + RhCl₃ + RhCl₃ (9)'</td>
<td>284.6</td>
<td>252.9</td>
<td>102.7</td>
<td>989.7</td>
<td>198.3</td>
<td>314.8</td>
<td>308.9</td>
</tr>
</tbody>
</table>

*aDiacetyl. *bBenzil. *cThe numbers in parentheses correspond to compounds of Table III.

Figure 6. Binding energy for Rh₃d of compounds (a) APS + RhCl₃, (b) APS + D + RhCl₃, (c) APS + B + RhCl₃, (d) APS + D + TEOS + RhCl₃, (e) APS + B + TEOS + RhCl₃.

Molecular Dynamics Simulation of the Temperature-Dependent Ionic Conductivity in Sodium(I)-β''-Alumina

Cathy Lane Rohrer* and Gregory C. Farrington*

Department of Materials Science and Engineering, University of Pennsylvania, 3231 Walnut Street, Philadelphia, Pennsylvania 19104

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Molecular dynamics (MD) simulation has been applied to a study of structure, ion motion, and superlattice formation in the fast ion conductor, sodium(I)-β''-alumina. The results reproduce, in a general way, the curved variation of ionic conductivity with temperature observed in an Arrhenius-type plot of single-crystal conductivity data for the compound. The curvature in the conductivity plot may be explained as resulting from an evolution in the conduction mechanism from a vacancy mechanism at high temperatures to highly correlated superlattice motion at lower temperatures. A correlation is seen between the location of Mg(II) ions in the spinel blocks and the ion/vacancy arrangement in the conduction layers.

Introduction

Developing the ability to design materials with specified properties is an intriguing goal, one which may become more attainable with the growing accessibility of fast computers. To achieve this goal, however, computer models must be developed which accurately reproduce experimentally observed properties of known materials before they can be trusted as design tools. β''-Alumina is a particularly good material for testing such models. Well-known for its ability to undergo ion exchange with a variety of mono-, di-, and trivalent cations, β''-alumina exhibits varied optical, structural, and transport properties depending on its mobile cation composition. It represents a good beginning challenge for simulation, since its composition and properties can be varied extensively without altering its structural framework. A reasonable computer model for β''-alumina should be able to reproduce the properties of its isomorphs.

This paper presents a study of the temperature-dependent ionic conductivity of pure sodium(I)-β''-alumina using molecular dynamics (MD) simulation. Prior studies of Na(I)-β'-alumina have shown that MD is effective as a structural probe, but its transport properties have not been accurately simulated for reasons both particular to the MD technique and to the structure of β''-alumina. For example, Wolf et al. encountered the limitations of the MD technique in their study of Na(I)-β''-alumina. The MD technique enforces periodic boundaries on the system being studied to avoid edge effects and more accurately represent long-range interatomic forces. Therefore, if the system under study has a tendency to order, as do the mobile ions in Na(I)-β''-alumina, the periodicity imposed by the MD technique must match the periodicity of the ordering under consideration. Otherwise, the MD-enforced periodicity will predominate over the system periodicity, and the atoms will never achieve an equilibrium configuration. As Wolf et al. noted in their work, their choice of MD "box" size, that is, the total number of unit cells explicitly included in the simulation, obstructed the mobile

# Table VI. Quantification of Surface Atomic Ratios

<table>
<thead>
<tr>
<th>compound</th>
<th>Si/N</th>
<th>N/Rh</th>
<th>Cl/Rh</th>
<th>Si/Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td>APS + RhCl</td>
<td>1.24</td>
<td>4.34</td>
<td>1.60</td>
<td>5.40</td>
</tr>
<tr>
<td>APS + D + RhCl</td>
<td>1.31</td>
<td>3.92</td>
<td>2.81</td>
<td>3.82</td>
</tr>
<tr>
<td>APS + B + RhCl</td>
<td>1.34</td>
<td>3.92</td>
<td>3.31</td>
<td>5.28</td>
</tr>
<tr>
<td>APS + D + TEOs + RhCl</td>
<td>4.98</td>
<td>3.12</td>
<td>3.02</td>
<td>15.21</td>
</tr>
<tr>
<td>APS + B + TEOs + RhCl</td>
<td>12.66</td>
<td>0.85</td>
<td>3.09</td>
<td>10.71</td>
</tr>
</tbody>
</table>

*The numbers in parentheses correspond to compounds of Table III.

Acknowledgment. This work was partially supported by the Comisión Interministerial de Ciencia y Tecnología, Spain (CICYT, project MAT88-017C02-02) and by the Fundación Ramón Areces. We express our appreciation to Dr. J. L. Fierro for his help in the XPS studies. Grateful acknowledgement is also due to Dr. J. Sanz for the 13C NMR spectra and to Dr. B. Casal for a critical reading of the manuscript.

Registry No. (EtO)2Si, 78-10-4; (EtO)2Si(CH3)2NH2, 919-30-2; PrNH2, 107-10-8; PhCOCOPh, 134-31-4; CH3COCH3, 431-03-8; NC,HCHO, 1121-60-4; PrN=CH(C2H5),=NHPr, 78788-23-5; PrN=CH(C6H5),=NHPr, 138936-96-3; PrN=CH2-py, 4206-52-4; SiO2, 7631-86-9; TEOS, 13463-22-9; RhCl(COD), 12095-47-6; RhCl(COD)(Et2O), 14871-47-7.


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